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CONDENSED MATTER

EPR-Determined Anisotropy of the *g*-Factor and Magnetostriction of a Cu_2MnBO_5 Single Crystal with a Ludwigite Structure

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Electron paramagnetic resonance (EPR) and magnetostriction of the Cu_2MnBO_5 single crystal have been studied. The EPR spectrum consists of a single Lorentzian line due to the exchange-coupled system of spins of Cu^{2+} and Mn^{3+} ions. It has been established experimentally that the *g*-factor in the paramagnetic region is strongly anisotropic and anomalously small, which is not typical of the exchange-coupled system of spins of Cu^{2+} and Mn^{3+} ions. At a temperature of 150 K, the *g*-factors along the crystallographic *a*, *b*, and *c* axes are 2.04, 1.96, and 1.87, respectively. Such small effective *g*-factor values can be due to the effect of the anisotropic Dzyaloshinskii–Moriya exchange interaction between the spins of Cu^{2+} and Mn^{3+} ions directed along the *a* axis. The presence of two Cu^{2+} and Mn^{3+} Jahn–Teller ions occupying four nonequivalent positions in the crystal is responsible for the absence of the inversion center. It is found that the behavior of the magnetostriction of Cu_2MnBO_5 is not typical of transition-metal crystals but is closer to the behavior of crystals containing rare-earth ions.

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The unusual properties of transition metal oxyborates with a ludwigite structure have attracted great attention of researchers in recent years [1–5]. Ludwigites are interesting in view of the variety of crystal structures having low-dimensional magnetism [6]. Experimentally, the microscopic magnetic structure was determined for Co_3BO_5, Fe_3BO_5 [3, 4, 7], and Cu_2MnBO_5 [8] oxyborates. The first two compounds have the space group *Pbam*, whereas Cu_2MnBO_5 belongs to the type of quasi-two-dimensional oxyborates with the ludwigite structure and, as all copper ludwigites, has a variant of the *Pbam* structure distorted because of the Jahn–Teller effect and the space group $P21/c$ [9]. In general, Cu_2MnBO_5 is so far the only ludwigite crystal containing various magnetic cations whose magnetic structure has been experimentally investigated [8]. Ions of transition metals with different valences, e.g., manganese and copper, can occupy four nonequivalent positions. In turn, this determines the physical properties of oxyborates with the ludwigite structure. The complex crystallographic structure and the presence of four nonequivalent positions occupied by magnetic cations lead to the appearance of an interesting magnetic structure, which can hardly be studied using integral techniques.

By studying the magnetic properties of the Cu_2MnBO_5 crystal, the orientation dependences of the inverse magnetic susceptibility with the transition temperature $T \sim 92$ K were obtained and interpreted. Experimental data for different crystallographic directions do not coincide in the paramagnetic phase; i.e., anisotropy is present possibly because of the strong anisotropy of the *g*-factor, which arises owing to the simultaneous presence of two Cu^{2+} and Mn^{3+} Jahn–Teller ions (Fig. 1). In order to determine the real values of the *g*-factor, we decided to study the EPR of the Cu_2MnBO_5 single crystal.

The Cu_2MnBO_5 ludwigite single crystal was grown by the flux method. The detailed growth conditions were described in [5]. The X-ray diffraction analysis showed no impurity phases. The magnetic properties of the prepared single crystal were studied on a PPMS-9 (Quantum Design) device and a vibrational magnetometer with a superconducting solenoid [10]. Magnetostriction was measured at the International Laboratory of Strong Magnetic Fields and Low Temperatures (Wroclaw, Poland) on a high-precision Andeen–Hagerling 2500A bridge in a facility with a superconducting solenoid (Oxford Cryogenic) within the known scheme [11] in the range of applied magnetic

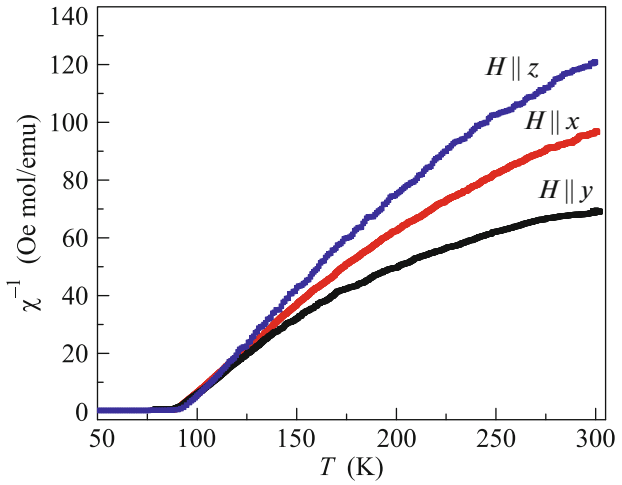

Fig. 1. (Color online) Temperature dependence of the inverse susceptibility of the $MnCu_2BO_5$ oxyborate single crystal with the ludwigite structure along three crystallographic axes.

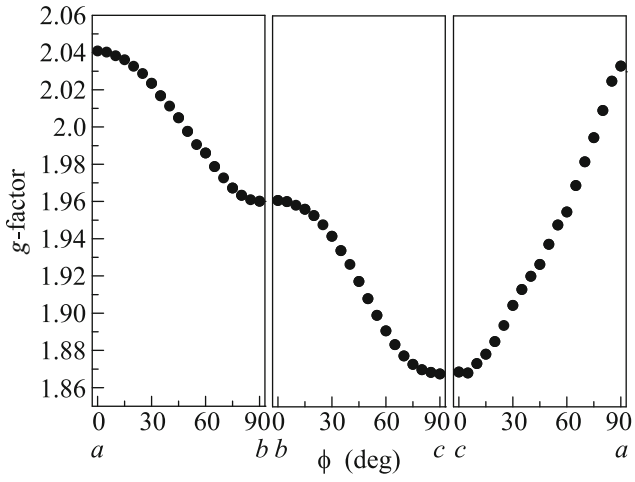

Fig. 2. Angular dependences of the effective g-factor in the (ab), (bc), and (ca) planes for the Cu_2MnBO_5 single crystal at a temperature of 150 K.

fields up to 14 T. Electron magnetic resonance measurements were carried out at the Zavoisky Physical-Technical Institute, Russian Academy of Sciences, using EMXplus and ELEXYS EPR spectrometers of the X (9.3 GHz) and Q (37 GHz) bands, respectively, in the temperature range of 4.2–300 K. The spectrometers were equipped with a goniometer, which made it possible to orient the investigated crystal with respect to the direction of the external magnetic field with a high accuracy.

The method for determining the anisotropic exchange parameters from the analysis of the angular dependences of the position and width of the EPR line in three mutually perpendicular planes for low-dimensional magnets was described in [12] and was applied for $CuGeO_3$, $LiCu_2O_2$ [13, 14], and other single crystals. The analysis of the angular dependences of the position and width of the EPR line makes it possible to accurately determine the directions of the principal axes of the g-tensor and the parameters of anisotropic exchange interactions in single-crystal samples. Accordingly, the angular dependence of the position of the resonance line was studied, and the angular dependence of the effective g-factor in Cu_2MnBO_5 ludwigites was obtained from the relation $h\nu = g_{\text{eff}}\beta H_{\text{res}}$, where ν is the microwave frequency and β is the Bohr magneton (Fig. 2).

In the paramagnetic region, the EPR spectrum consists of a single Lorentzian line being a superposition of absorption lines of Cu^{2+} and Mn^{3+} ions. The anisotropy of the effective g-factor was determined using the data obtained from angular dependences of the resonance field of EPR spectra. The resulting angular dependences of the effective g-factor at a temperature of 150 K are presented in Fig. 2. The effective g-factor values along the crystallographic a, b, and c axes are 2.04, 1.96, and 1.87, respectively. These values are anomalously small for the exchange-coupled system of the spins of Cu^{2+} and Mn^{3+} ions, whose g-factor should be $[2g(Cu^{2+}) + g(Mn^{3+})]/3$.

Such small effective g-factors can be due to the formation of low-symmetry clusters of Cu^{2+} and Mn^{3+} ions having a short-range magnetic order [15, 16]. The absence of the inversion center is associated with the presence of two Cu^{2+} and Mn^{3+} Jahn–Teller ions occupying four nonequivalent positions in the crystal. The strong distortion of oxygen octahedra removes the degeneracy of the upper, twofold degenerate, level of the Cu^{2+} ion in the ^2D state and reduces the symmetry of the nearest environment. In turn, the low symmetry and absence of the inversion center leads to the appearance of the antisymmetric Dzyaloshinskii–Moriya exchange, which determines the structure of the short-range magnetic order of clusters consisting of Cu^{2+} and Mn^{3+} ions.

The presence of the short-range magnetic order in the paramagnetic region is in good agreement with the deviation of the inverse magnetic susceptibility from the Curie–Weiss law (see Fig. 1) and the strong anisotropy of the g-factor near the transition to the magnetically ordered state (Fig. 3).

It follows from the temperature dependences of the effective g-factor along the crystallographic b and c axes (Fig. 3) that the anisotropy of the g-factor increases when approaching the temperature of the magnetic phase transition, and the g-factors along the crystallographic b and c axes at a temperature of 100 K are 2.8 and 1.6, respectively. It is difficult to explain such a large difference in g-factors within the framework of the crystal anisotropy. Apparently, at temperatures close to the magnetic phase transition tempera-

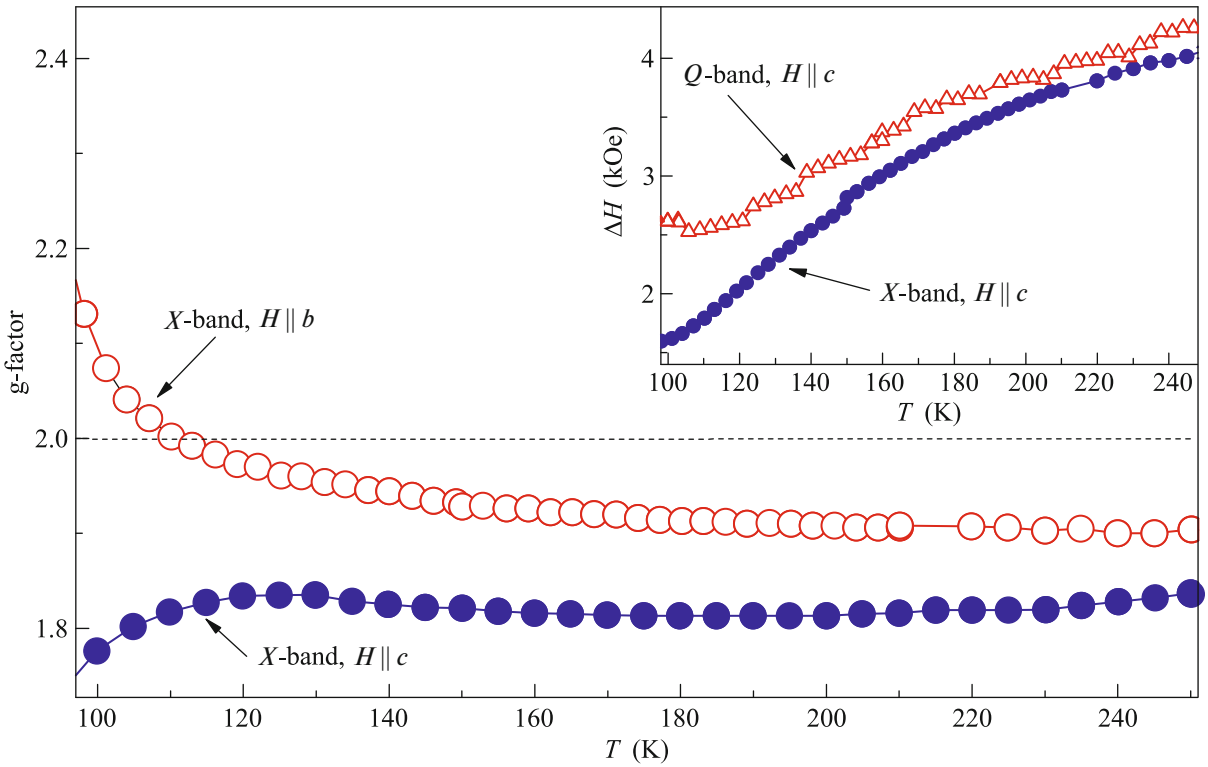

Fig. 3. (Color online) Temperature dependence of the parameters of the EPR line of Cu_2MnBO_5. The inset shows the temperature dependence of the magnetic resonance linewidth in the *X* and *Q* bands.

ture, which is 92 K [8], partial magnetic ordering occurs, which leads to the appearance of chains or even planes with a long-range magnetic order.

In addition, our study of the EPR spectra show that the magnetic resonance linewidth measured in the *Q* band at a temperature of 100 K is larger than that in the *X* band by 200 Oe (inset, Fig. 3). This fact may indicate the presence of a significant magnetostriction effect because of the Dzyaloshinskii–Moriya interaction in the Cu_2MnBO_5 crystal, which, finally, leads to the shift in the positions of atoms at the increase in the magnetic field in the *Q* band. In view of this circumstance, the magnetostriction of this crystal was measured (Fig. 4).

In general, the magnetostriction of this crystal has an unusual form: the crystal for the configuration $\Delta L \parallel H \parallel c$ is first compressed along the *c* axis and, then, begins to expand when the field exceeds ~5 T. At the same time, the magnetostriction curves for the configuration $\Delta L \parallel c \perp H$ have the usual quadratic form. This behavior is not typical of transition-metal crystals but is closer to the behavior of crystals containing rare-earth ions [17, 18]. A more detailed analysis of the magnetostriction curves requires additional calculations.

The EPR study indicates the presence of the anisotropy of the *g*-factor in the Cu_2MnBO_5 crystal. The effective *g*-factor values along the crystallographic *a*, *b*, and *c* axes at a temperature of 150 K are anomalously small for the exchange-coupled system of the spins of Cu^{2+} and Mn^{3+} ions and are 2.04, 1.96, and 1.87, respectively. Such small effective *g*-factor values can be due to the formation of clusters of copper and manganese ions whose magnetic structure is determined by the antisymmetric Dzyaloshinskii–Moriya exchange. The temperature dependences of the *g*-factor for the crystallographic *b* and *c* axes indicate that partial magnetic ordering occurs at temperatures close to the magnetic phase transition temperature, which leads to the appearance of chains or even planes with the long-range magnetic order of exchange-coupled spins through oxygen ions.

The dependences of magnetostriction in a wide range of applied magnetic fields to ~15 T were also obtained. The behavior of the magnetostriction of the given crystal is very nontrivial. Under conditions of longitudinal magnetostriction, the crystal is first contracted along the *c* axis and is then expanded when the magnetic field exceeds ~5 T. Such unusual behavior requires further studies and calculations.

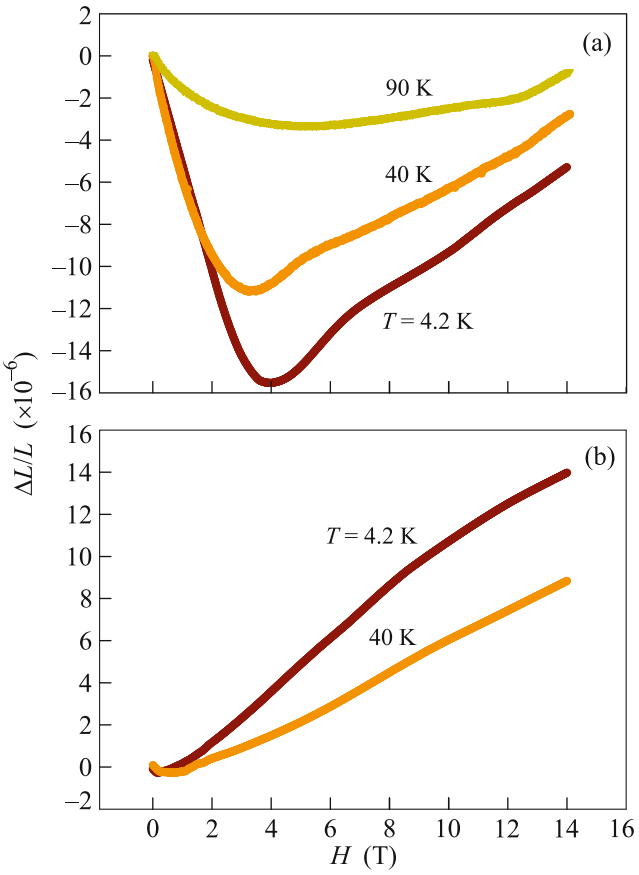

Fig. 4. (Color online) Magnetostriction of the Cu_2MnBO_5 crystal in the configurations (a) $\Delta L \parallel H \parallel c$ and (b) $\Delta L \parallel c \perp H$.

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